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Research on band-edge emission properties and mechanism of high-quality single-crystal diamond

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ABSTRACT

The band-edge emission properties from a homoepitaxial chemical vapor deposition single-crystal diamond have been studied in detail through photoluminescence (PL) measurement from room temperature down to 8 K. In particular, we firstly observed the third phonon replica of the intrinsic emission at 5.277 eV and the second phonon replica of the intrinsic emission at 5.330 eV in the PL spectra, indicating the high crystallinity of our diamond sample. The main optical characteristics of intrinsic recombination radiation for single crystal diamond at low temperatures have been reported and its light emission mechanism has been discussed in this paper.

1. Introduction

In recent years, the growth and physical properties of wide-band gap materials have been intensively investigated in various research areas such as electronics, optics, thermotics and acoustics. As one of the most important wide-band gap materials, diamond has an indirect gap of 5.5 eV, and is considered to be a promising candidate for high frequency, high temperature and high power semiconductor devices [1–6] due to its outstanding material properties such as high mobility (4500 $cm^2/(V\cdot s)$ and 3800 $cm^2/(V\cdot s)$ for electrons and holes, respectively), high drift velocity (0.85×10^7-1.2×10^7 cm/s and 1.5×10^7-2.7×10^7 cm/s for electrons and holes, respectively) [1,7,8], high breakdown field (>10 MV/cm) and low dielectric constant (5.7) [9]. In addition, compared with other major high-mobility semiconductors available at present, diamond has a large exciton binding energy of 80 meV, so that not only free carriers but also excitons stably exist at room temperature [10,11]. Consequently, the band-edge emission of diamond can be observed up to higher temperatures. The band-edge emission due to exciton recombination following the irradiation with high-energy photons or electrons is particularly sensitive to the presence of defects in diamond crystal, so they could only be observed in the diamond samples of extremely high crystalline perfection [12].

The research on the band-edge emission in diamond crystal has been conducted since 1965, when Dean analyzed the intrinsic and extrinsic recombination radiation from natural and synthetic aluminum-doped diamond [13]. In 1989, the band-edge emission due to free-exciton recombination radiation associated with momentum-conserving phonons at 5.32 eV, 5.27 eV and 5.25 eV were observed by Collins et al. [14]. In the following years, the research on bound-exciton recombination has been studied through cathodoluminescence measurements by Kawarada et al. [15–17]. Moreover, the phonon replicas of excitonic emission at 5.27 eV and the phenomenon that exciton lifetime exhibits a non-monotonic dependence on the sample temperature have been studied by Donato et al. [18]. Despite these previous research efforts, the properties of band-edge emission in single-crystal diamond are not completely understood as yet, and further explanation will still be required.

Both cathodoluminescence (CL) and photoluminescence (PL) should be the major techniques for the study of the band-edge emission in diamond [19]. However, most of the investigations on the band-edge emission in diamond have been performed by using

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the CL measurement; in comparison, much less work has been done by the means of PL measurement because that optical excitation is difficult in PL due to the band gap width of the diamond. However, the electron beam used in the CL measurement will invariably induce a certain amount of crystalline defects inside the diamond sample, whereas the PL measurement is nondestructive to diamond samples [20], which is much more ideal for the relevant investigation. In this paper, we apply the PL measurement to study the band-edge emission in the temperature range from 8 K to 300 K. The third phonon replica of the intrinsic emission at 5.277 eV and the second phonon replica of the intrinsic emission at 5.330 eV in diamond crystal have been first observed.

2. Experimental

A high-quality diamond specimen with a thickness of 600 μm, was prepared using a high methane concentration ratio (CH_4/H_2) of 6% in a microwave plasma chemical vapor deposition (MPCVD) reactor (AX5250S) onto the (001)-oriented high-pressure and high-temperature (HPHT)-synthetic single-crystal diamond substrates with dimensions in the region of 3 mm × 3 mm × 1 mm. The total gas pressure, microwave power, and substrate temperature were 120 Torr, 5000 W and 1100 °C, respectively.

The optical measurements were carried out mainly through both the Raman and PL measurements. The Raman spectra were obtained at room temperature from a micro-confocal Raman spectrometer manufactured by Renishaw with the spectral resolution of 1 cm^{-1} and the excitation wavelength of 633 nm. A monochrometer with an 1800 grooves/mm grating was used for the measurements. PL measurements were carried out in a home-made DUV laser spectroscopy system equipped with a frequency-quadrupled Ti: sapphire laser, which supplies as an excitation wavelength of 213 nm at a 76 MHz repetition rate. The diamond sample was fixed in the copper sample holder placed inside a closed-cycle Helium refrigerator. The PL spectrum from the diamond sample with temperature varying from 8 to 300 K were collected by a parabolic aluminum mirror, transmitting through a quartz window and a set of focusing lenses into a monochromator. A photomultiplier tube was used as the detector. The diameter of focused excitation spot is less than 100 μm and the excitation power is 40 mW.

3. Results and discussion

The Raman spectra from both the diamond specimen and its substrate were shown in Fig. 1. A sharp first order Raman line of diamond at 1332.7 cm^{-1} can be clearly observed in the figure. The value of the peak position of the diamond sample is comparable to its substrate standard value (1332.6 cm^{-1}). The full width at half maximum (FWHM) of the spectra from the diamond sample and substrate is 2.0 cm^{-1} and 2.8 cm^{-1}, respectively. The small shift of the peak position and narrow linewidth in the Raman spectra reveals a rather high perfection of the crystal lattice with a low amount of residual stress in the diamond sample [12,21,22].

In Raman spectra as previously reported in the literature, a single peak at 1581 cm^{-1} and two broadbands centered around 1360 cm^{-1} and 1590 cm^{-1} are usually observed when there exist glassy carbon and pyrolytic graphite consisting of amorphous sp^2 structures [23]. However, in the Raman spectra of our diamond sample, only one peak at 1332.7 cm^{-1} can be observed, as shown in Fig. 1, which should indicate the high quality of our diamond sample.

Fig. 2 shows the PL spectrum of homoepitaxial diamond film measured at 8 K, where both the band-edge emission and defect luminescence can be observed. As shown in the spectrum, the

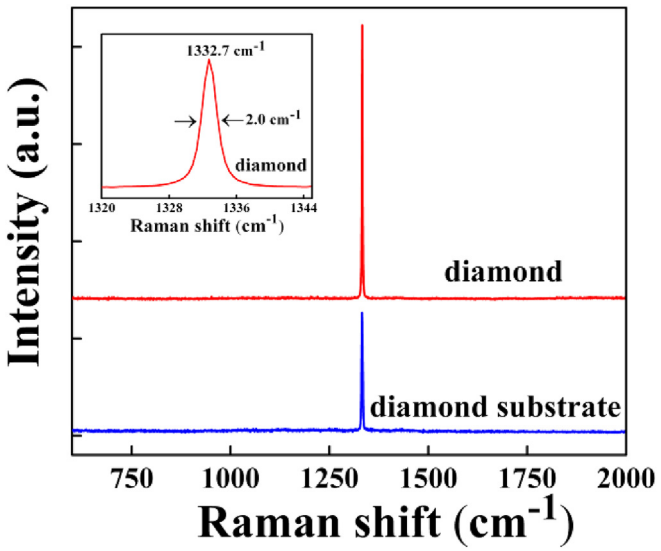

Fig. 1. Raman spectra of the single-crystal diamond specimen and its substrate, as obtained at room temperature, with the FWHM and peak position of diamond being shown in the inset. (A colour version of this figure can be viewed online.)

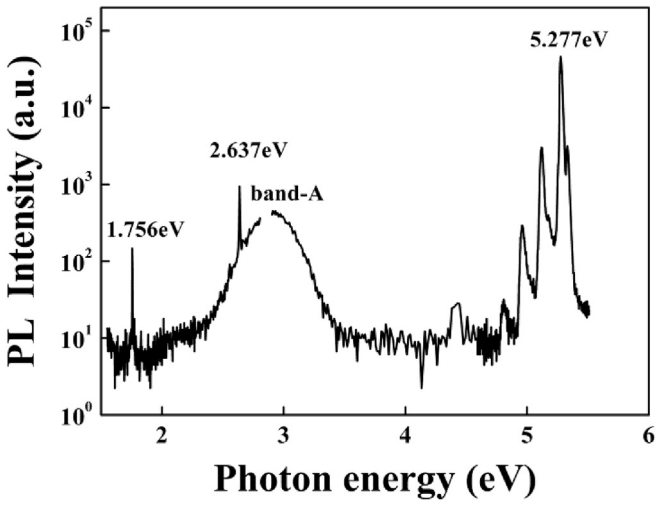

Fig. 2. PL spectra of diamond measured at 8 K from 1.5 to 5.5 eV energy.

4.8–5.5 eV lines are caused by the near-band-gap emission [24]. In particular, the 4.800 eV line in the spectrum should be identified as the third phonon replica of the intrinsic emission at 5.277 eV, which is first observed in the homoepitaxial diamond film, to our best knowledge. 2.637 eV line and 1.756 eV line are the secondary and tertiary diffraction peak of 5.277 eV, respectively. Besides, 4.400 eV line should be relevant to nitrogen impurities [25]. The band-A (2.900 eV) due to closely spaced donor-acceptor (D-A) pairs is directly correlated with dislocations [26].

The near-band-gap emission of diamond at 8 K with Gaussian fitting was plotted in Fig. 3. In the spectrum, eight peaks can be clearly observed at 5.330 eV (A1), 5.175 eV (A2), 5.020 eV (A3), 5.277 eV (B1), 5.116 eV (B2), 4.957 eV (B3), 4.800 eV (B4) and 5.255 eV (C1), respectively. Their energy positions, FWHMs and integral intensities are listed in Table 1.

For ultra-pure diamond at low temperatures, a narrow-line spectrum of intrinsic recombination radiation is usually observed due to exciton recombination [13]. The physical process is that free